

Bismuth Dissolution from Smelter Flue Dust Residues

by J. D. Miller, J. A. Herbst, and J. L. Sepulveda

Effective bismuth removal from flue dust residues has been accomplished for flue dusts from both zinc and copper smelters. Selective dissolution of bismuth, with respect to silver and lead, can be achieved by the proper manipulation of temperature, sulfuric acid addition and sodium chloride addition. Optimum levels of these variables were determined using a response surface technique to maximize the objective function: $Y = \%Bi/(1 + \%Ag)$. In the case of the flue dust residue from a zinc smelter, which contains bismuth as an impurity (0.05%), 86% bismuth removal can be realized with less than 1% combined silver and lead dissolution. Similarly, in the case of flue dust from a copper smelter, which contains bismuth as a primary constituent (3.3%), 93% bismuth removal was obtained with little dissolution of silver and lead values.

The processing of residues derived from various operations in the mining and metallurgical industry for byproduct recovery is becoming more prevalent. A principal target for byproduct recovery is flue dust produced by conventional smelting operations. Flue dust from zinc smelters has been processed for many years for the recovery of cadmium.^{1,2} The cadmium recovery technique which consists of a selective sulfation roast, followed by a water leach and zinc dust cementation, produces a lead cake residue (see chemical analysis in Table 1), which consists primarily of lead sulfate.

The high silver content, of approximately 100 per oz ton, makes lead cake a potentially valuable product. However, bismuth, even at levels of 0.05%, frequently limits the marketability of this material as lead smelter feed. In this and other systems, the selective removal of bismuth from such residues is of considerable interest.

The intent of this investigation was to determine the conditions under which selective bismuth removal from flue dust residues can be achieved. A hydrometallurgical approach for bismuth removal from lead cake was selected for detailed study.^{3,4,5} In this particular case the objective was to selectively dissolve the bismuth and minimize the extent of lead and silver dissolution. The low solubility of lead sulfate in sulfuric acid solution and the high stability of bismuth chloride complexes suggested that an acidic chloride leach might be effective for this purpose. Statistically designed, bench scale leaching experiments were initiated to test this hypothesis for lead cake processing. In addition, a cursory examination was made of the applicability of this technique for the treatment of copper smelter flue dust.

Experimental Materials and Technique

The lead cake used in this study was obtained from St. Joe Minerals Corp. zinc smelter in Monaca, Pa. The sample was received as a mud containing 85% by weight solids. Core samples of the feed stock, which were used for leaching experiments, revealed that the lead cake was well mixed both with respect to the particle size distribution and the chemical composition. X-ray diffraction analysis of lead cake revealed the major compound to be lead sulfate. The chemical state of bismuth and silver could not be determined due to their low concentrations. Size analysis performed with a Warman Cyclometer showed that the size distribution of the solids was well characterized by a Gates-Gaudin-Schuhmann distribution with a size modulus of 35μ and a distribution modulus of 0.39.

J. D. MILLER, J. A. HERBST, Members SME, are Associate Professors of Metallurgy, J. L. SEPULVEDA, Member SME, is a graduate student, all University of Utah, Salt Lake City. SME Preprint 75B353, SME Fall Meeting, Salt Lake City, Utah, Sep. 1975. Manuscript, Aug. 6, 1975. Discussion of this paper submitted in duplicated prior to Sep. 15, 1976, will appear in SME Transactions, December 1976 and in AIME Transactions, 1976, Vol. 260.

The leaching experiments were performed in an unbaffled two-liter spherical reactor agitated with a single blade impeller at a speed of 300 rpm. The reactor was submerged in a constant temperature oil bath. The leach solution occupied a reactor volume of 1.5l; the initial solids concentration was 5% by weight. Samples of the leach liquor were withdrawn at predetermined intervals (0.25, 1, 4, and, 16 hr) and analyzed by atomic absorption spectroscopy.

Empirical Modeling and Optimization

Three variables were manipulated in these experiments: temperature, sulfuric acid addition, and sodium chloride addition. Conditions were sought which resulted in the maximum recovery of silver and lead in the residue and maximum bismuth removal. The results of preliminary experiments at 70°C (Table 2) indicated that a minimum sodium chloride addition of 0.1M was required in order to exceed 75% bismuth removal. Other data showed that satisfactory results could also be achieved at 50°C with 0.5M H₂SO₄ and 1.0M NaCl. Practical constraints from an operating standpoint require that temperatures do not exceed 70°C, that the H₂SO₄ addition be less than 1.0M, and that the NaCl addition be less than 2.0M. These constraints arise from equipment corrosion and waste disposal considerations. These data and constraints provided the starting point for a search to identify optimum operating conditions for this extraction process.

In order to identify the levels of the three variables which would result in an optimum separation, a response surface method^{6,7} was employed to plan and analyze all additional

Table 1. Chemical Composition of Lead Cake Residue

Element	Content
Pb	37.73%
Ag	149.70 oz per ton
Zn	4.93%
In	0.24%
Bi	0.051%
Cd	0.86%
Cu	0.95%
Sb	0.019%
As	0.065%
In	0.015%

Table 2. Preliminary Experiments to Define the Effect of Small Additions of Sodium Chloride

NaCl (M)	(70°C, 0.5M H ₂ SO ₄ , 300 rpm)		
	Percent Dissolved After 16 hr		
	Bi	Ag	Pb
0	52.73	.24*	0.10*
0.05	72.27	.24	0.11
0.10	80.86	.28	0.10

* Extrapolated value

TWO LEVEL FACTORIAL DESIGN

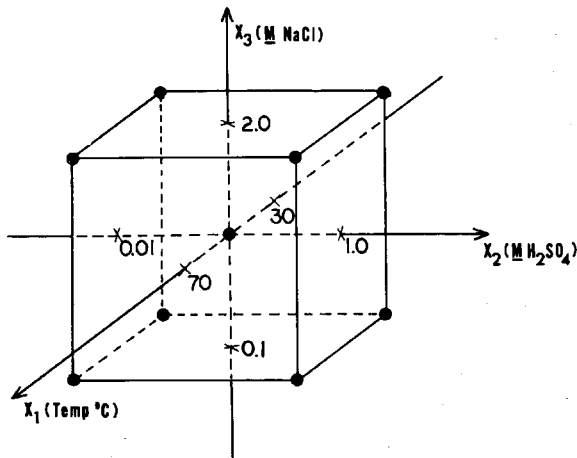


Fig. 1—Two-level, three-dimensional, factorial design with center point replication. Solid circles represent position of experiments. X_1 —Temperature ($^{\circ}$ C). X_2 —Sulfuric acid concentration (M). X_3 —Sodium chloride concentration (M).

experiments. This approach involves designing a set of experiments which permits the building of an empirical model(s) to represent in a quantitative fashion the effect of each of the variables and their interactions on the extraction response. In turn, standard optimization algorithms can be used in conjunction with the fitted empirical models to determine the optimum levels of operating variables subject to any constraints imposed on the system.

In this particular case, a 2^3 factorial experimental design with center point replication⁶ was used to fit the model:

$$Y = \frac{\%Bi}{1 + \%Ag} = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_1 X_2 + \beta_5 X_1 X_3 + \beta_6 X_2 X_3 + \beta_7 X_1 X_2 X_3 \quad (1)$$

where X_1 is the reaction temperature ($^{\circ}$ C), X_2 is the acid addition (M), X_3 is the sodium chloride addition (M), and $\beta_0, \beta_1, \dots, \beta_7$ are adjustable constants. The system response, Y , was chosen in such way that it measures the selectivity of bismuth removal with respect to silver. Complete removal of bismuth with all the silver remaining in the residue yields a value of $Y = 100$, while complete dissolution of the silver with no bismuth removal yields a value of $Y = 0$.

The experimental design employed was centered around the point $(X_1, X_2, X_3) = (50^{\circ}\text{C}, 0.505\text{M}, 1.05\text{M})$ with peripheral

Table 3. Statistical Analysis of Acid Chloride Leaching of Lead Cake

2^3 Factorial Design:

Factors

X_1 : Temperature $^{\circ}$ C
 X_2 : Sulfuric Acid Concentration M
 X_3 : Sodium Chloride Concentration M

Factorial Levels	Percent Dissolved, 16 hr			Experimental Response, Y	Predicted Response \bar{Y}	
	X_1	X_2	X_3			
30 0.01 0.1	Bi	Ag	Pb	Zn	1.50	1.29
70 0.01 0.1	1.95	0.35	0.07	23.35	1.44	1.24
30 1.0 0.1	46.09	0.15	0.06	35.53	40.08	39.87
70 1.0 0.1	86.33	0.35	0.09	63.95	63.95	63.74
30 0.01 2.0	38.28	10.52	7.85	21.56	3.32	3.12
70 0.01 2.0	44.92	6.0	7.95	25.38	6.42	6.21
30 1.0 2.0	56.64	11.69	1.02	31.97	4.46	4.26
70 1.0 2.0	89.84	14.22	4.77	80.19	5.90	5.70
50 0.505 1.05	82.03	4.48	0.42	48.72	14.97	15.68
50 0.505 1.05	82.03	4.67	0.56	48.21	14.47	15.68
50 0.505 1.05	78.13	3.90	1.19	53.80	15.94	15.68

Model:

$$Y = \frac{\%Bi}{1 + \%Ag} = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_1 X_2 + \beta_5 X_1 X_3 + \beta_6 X_2 X_3 + \beta_7 X_1 X_2 X_3$$

$$\bar{Y} = 1.145 - 0.01192X_1 + 21.81X_2 - 0.1869X_3 + 0.6382X_1 X_2 + 0.04484X_1 X_3 - 9.704X_2 X_3 - 0.34X_1 X_2 X_3$$

Test for "Goodness of fit" showed the model to be acceptable at the 75% level and above.

points as shown in Fig. 1. Experimental results obtained for each combination of three variables after 16 hr of leaching are shown in Table 3 along with the fitted values of $\beta_0, \beta_1, \dots, \beta_7$ obtained by linear regression from this data. It is significant to note that the extent of dissolution of the principal components (Bi, Ag, Pb, Zn) varies widely for the range of variables considered. Fig. 2 shows the "one variable at a time" response of this leaching system to changes in temperature, acid additions, and NaCl additions. Data obtained from the experimental design and the values predicted from the empirical equation are plotted here for comparison. In all instances the predictions appear to be in good agreement with the experimental values.

Table 4 shows the analysis of variance^{6,9} used to test the "goodness of fit" of the empirical model to the experimental data and the significance of the effects of the three variables and their interactions on the system response. The hypothesis which supposes the fitted model describes the data within the limits of experimental error can be accepted at the 75% level and above. Subsequent tests to determine whether the model could be reduced by the elimination of any of three variables or their interactions showed that each of the main effects and interactions was highly significant, indicating the full model was required to describe the data.

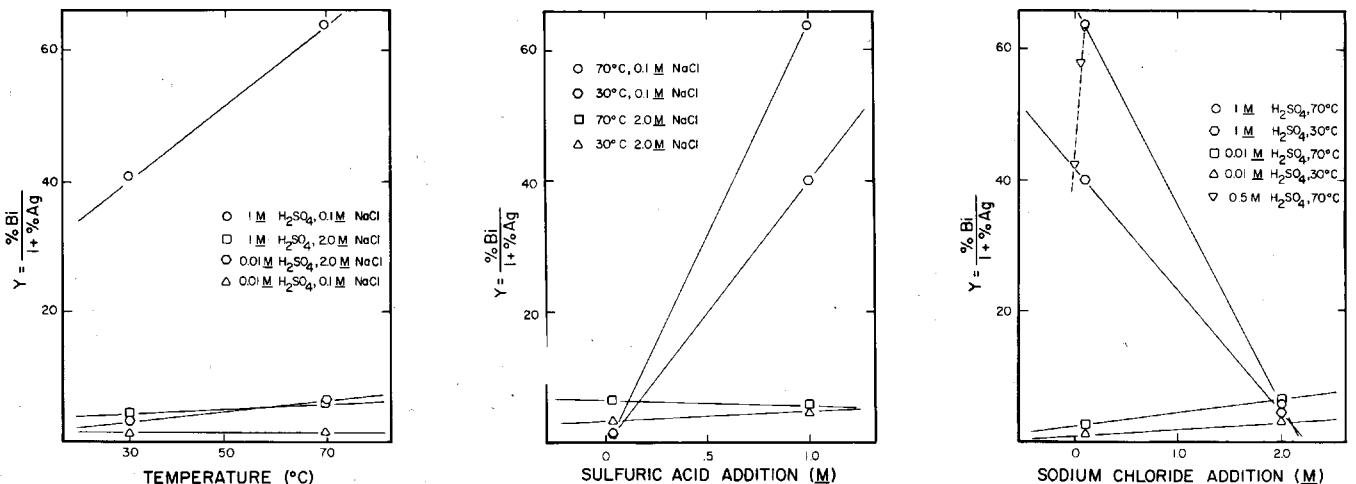


Fig. 2—Response of leaching system to changes in temperature, acid additions, and NaCl additions. Symbols represent experimental values. Solid lines represent empirical model predictions.

Table 4. Analysis of Variance for the Design 2^{3}**

Source of Variation	Sum of Squares	d.f.	Mean Square	F = $\frac{\text{Mean square Effect}}{\text{Mean square Residuals}}$
Effect of removing				
X ₁	100.4	1	100.4	125.5*
X ₂	1293.1	1	1293.1	1616.4*
X ₃	943.2	1	943.2	1179.0*
X ₁ X ₂	62.0	1	62.0	77.5*
X ₁ X ₃	46.5	1	46.5	58.1*
X ₂ X ₃	1261.4	1	1261.4	1576.8*
X ₁ X ₂ X ₃	81.8	1	81.8	102.3*
Subtotal (Regression)	3788.4	7	541.2	
Deviations about the regression "line"				
Experimental error	1.3	1	1.3	
Subtotal (residual)	1.1	2	0.6	
Total (Adjusted)	3790.8	10	379.1	

* Significant at 99.5% confidence level ($F_{0.005}(1,3) = 55.6$)
 ** See references 6 and 9.

Because of the large number of parameters in the empirical model, the power* of the test for goodness of fit is not very high.⁶ A further attempt to verify the model by comparing the experimental response at (70, 0.5, 0.1) with the predicted response suggested that this very simple model may be inadequate for truly accurate predictions. These results suggested that the introduction of quadratic terms in Eq. 1 may improve its predictive capability. Additional experiments required to expand the model to include quadratic terms were not deemed justified in the present study.

It is quite evident from Fig. 2 that optimum extraction conditions exist at high temperature, high acid additions, and low chloride additions. In the absence of interactions (X₁X₂, X₁X₃, X₂X₃, X₁X₂X₃ terms), linear programming theory¹⁰ states that the optimum can be found at the intersection of constraints. It is not obvious a priori to what extent the response surface represented by the fitted model is distorted from planar by the interaction terms, hence the exact location of the optimum is not evident.

The curvature imparted to the response surface by the interaction terms is depicted graphically in Fig. 3 for constant contours of the objective function equal to 10, 30, 50, and 60.

In order to precisely locate the optimum, two nonlinear constrained optimization techniques were explored, i.e., Flexplex¹¹ and Direct Search.⁶ In each case maximization of the fitted response subject to the previously specified constraints resulted in an optimum value of Y = 63.74 at the point X₁ = 70°C, X₂ = 1M H₂SO₄ and X₃ = 0.1M NaCl (Fig. 3). Since this set of conditions corresponded to a point in the experimental design and the experimental value of Y = 63.95 is in good agreement with the predicted value, this point was accepted as the "best" set of operating conditions which satisfied the constraints. In terms of the distribution of individual species these conditions yield a highly desirable response. Specifically, 86% of the bismuth and 64% of the zinc have been extracted while greater than 99% of both lead and silver have been retained in the residue.

Discussion

Leaching Reaction Chemistry: Although most of the metallic constituents of lead cake form complex chloro-anions as evidenced by the stability constants given in Table 5,¹² the lead complexes are generally less stable than the other complexes. This condition coupled with the low solubility of PbSO₄ in sulfuric acid solutions suggests that lead solubility will be low in sulfuric acid solutions containing small

* The power of the test is the probability of rejecting the model given that it is incorrect.

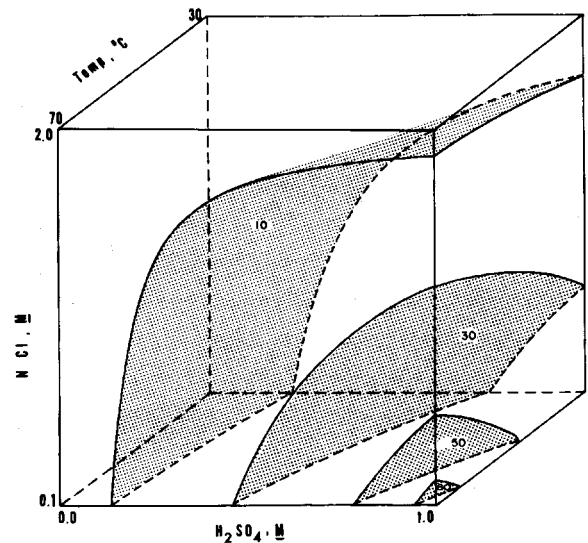


Fig. 3—Response surface contours calculated from the fitted model for various values of the objective function, Y = %Bi(1 + %Ag.)

additions of sodium chloride; indeed Larson¹³ has observed such an effect. However, Marsden¹⁴ found that significant dissolution of lead sulfate may occur in sulfuric acid solutions provided high concentrations of sodium chloride (300 gpl) are used.

On the other hand, bismuth and silver both form strong complex chloro-anions suggesting that a selective separation between the two would be impossible. Such would be the case only if the chemical potential of each component in the solid phase were equivalent and if dissolution rates were the same. Although the solid solubility of bismuth and silver in the lead sulfide lattice is well known,¹⁵ the disposition and chemical potential of these components in a lead sulfate matrix has not been determined. If the bismuth and silver assume a chemical potential similar to that which exists in their respective oxides or sulfates, then simultaneous dissolution of both components in an acidic chloride leach should occur.

The experimental results shown in Table 3 and plotted in Fig. 2 illustrate that selective dissolution of bismuth can be achieved. This fact probably indicates a difference in the solid state activity of the bismuth and silver. The bismuth appears to be more accessible, whereas the silver may remain in an unclustered state similar to a solid solution condition which could account for its limited solubility. It is apparent from the data that lead and silver dissolution is most sensitive to chloride additions and that extensive dissolution of these species only occurs at high chloride levels. Temperature and sulfuric acid addition are of secondary importance. These observations tend to support the concept of intimate lead and silver association in the lead sulfate matrix.

In contrast to lead and silver dissolution, bismuth extraction is strongly dependent on sulfuric acid addition. The acid sensitivity suggests that bismuth may be present in the oxide state. Bismuth dissolution initially has a strong dependence on chloride addition, however for concentrations in excess of 0.1M no further enhancement is achieved since the chloride demand by the bismuth has been satisfied.

Table 5. Stepwise Formation Constants for Complex Chloro-Anions¹² Log Equilibrium Constant

Element	K ₁	K ₂	K ₃	K ₄	K ₅	Ionic Strength
Ag ⁺	2.85	1.87	0.32	0.86		0.2M NaCl
Bi ³⁺	2.09	1.81	1.50	1.47	0.81	3.0M NaClO ₄
Cd ²⁺	1.32	0.90	0.09	-0.45		4.5M NaClO ₄
Cu ²⁺	2.80	1.60	0.49	0.73		variable
In ³⁺	1.42	0.81	1.00	-0.2		1.0M NaClO ₄
Pb ²⁺	0.88	0.61	-0.40	-0.15		1.0M KCl
Zn ²⁺	-0.32	0.27	-0.25	0.15		4.5M ionic strength

Table 6. Chemical Composition of Copper Smelter Flue Dust

Element	Content
Bi	3.25%
Ag	12.25 oz per ton
Zn	3.25%
Pb	39.48%
Cu	7.25%

Table 7. Acid Chloride Leach of Copper Flue Dust

Experimental Conditions	Time, Hr	Percent Dissolved at Time t				
		Bi	Ag	Pb	Zn	Cu
95°C	.167	59.59	3.82	0.13	94.69	77.41
1.0M H ₂ SO ₄	1	65.43	1.85	0.11	97.61	83.97
0.1M NaCl	2	66.60	1.85	0.12	98.20	86.59
	4	79.45	1.72	0.10	99.37	87.90
95°C	.167	68.94	2.49	0.09	100.00	80.03
1.0M H ₂ SO ₄	1	81.79	2.49	0.08	100.00	83.97
0.2M NaCl	2	88.80	2.49	0.10	100.00	83.97
	4	93.48	3.39	0.10	100.00	90.53

Experimental Conditions: 300 rpm
79 grs of solids in 1500 ml of leaching solution.

Applications: Selective bismuth removal from lead cake is demonstrated by the previous results in which optimum conditions of 70°C, 1M H₂SO₄ and 0.1M NaCl resulted in 86.33% bismuth removal and a recovery of 99.65% silver in the residue.

The optimum conditions represent rather high levels of temperature and acid addition in order to achieve a maximum bismuth removal of 85%. If a higher level of residual bismuth could be tolerated, less severe leaching conditions could be employed. For example, if a reduction in bismuth content to only 0.02% were required, as specified by some smelters, the desired results could be achieved at 50°C and at half the acid addition.

To further test the generality of the acidic chloride leach technique for the selective dissolution of bismuth with respect to silver, flue dust from a copper smelter was obtained. The chemical composition of this material (Table 6) differed significantly with respect to bismuth, copper, and silver content when compared to lead cake obtained from the zinc smelter. However, the flue dusts were similar in that the lead (approximately 40% in each case) was present as PbSO₄. It should be noted that bismuth concentration is high enough to warrant its recovery as a primary product rather than disposal as an impurity (0.05% Bi) as in the case of lead cake processing.

Similar to the system response for lead cake, excellent bismuth dissolution was attained by an elevated tempera-

ture, acid chloride leach. The same experimental technique was used and similar experimental results were obtained.

Results obtained at 95°C and 1.0M sulfuric acid at different chloride levels are given in Table 7. It was found that a chloride addition similar to that used for the lead cake leach was all that was necessary even though the bismuth level (3.3%) in the copper smelter flue dust was significantly higher than the bismuth level (0.05%) in the lead cake. The silver release was found to be higher from the copper flue dust; however, for 93% bismuth extraction the silver recovery in the residue was still greater than 96%.

Conclusions

To date, the acidic chloride leach has been applied successfully to flue dust residues from zinc and copper smelters but in general it could be used to selectively dissolve bismuth with respect to silver from oxidized particulate materials such as waste products and roasted concentrates. Research has clearly demonstrated the critical nature of the chloride addition in order to achieve the desired selectivity.

Acknowledgments

The authors wish to acknowledge funding of this research program by St. Joe Mineral Corp. Discussion with A. O. Martel, A. D. Zunkel, and T. Janeck, all of St. Joe, contributed significantly to the success of this program.

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